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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :		(11) International Publication Number: WO 93/06470
G01N 23/227, G01T 1/24	A1	(43) International Publication Date: 1 April 1993 (01.04.93)

(21) International Application Number: PCT/EP91/01771

(22) International Filing Date: 17 September 1991 (17.09.91)

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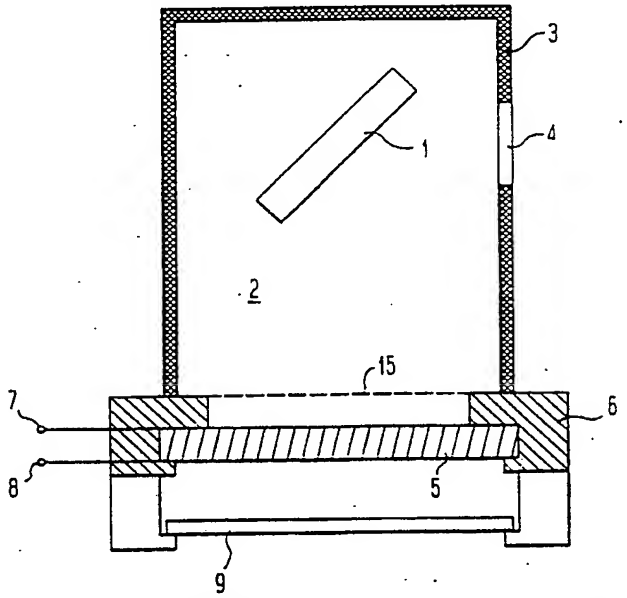
(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, NL, SE).

Published
With international search report.

(54) Title: ELECTRON DETECTOR DEVICE FOR SPECTROSCOPIC ANALYSES OF SURFACES UNDER X-RAY EXCITATION



(57) Abstract

This invention concerns an electron detector device for spectroscopic analyses of surfaces under monochromatic X-ray excitation, this detector comprising: (i) a silicon diode (9) which is able to detect with a gain ≥ 1 accelerated secondary electrons; (ii) a microchannel plate (5) to pre-amplify the conversion photoelectrons emitted by the sample (1), and which is used at extremely low gain but with excellent linearity characteristics. The key component is a cooled Si-diode made of high resistivity n-type silicon with an ion implanted p^+ layer (11) which is about 1300 Å thick. Its performances in detecting energetic electrons result from the absence of additional dead layers (passivated SiO_2 or protective aluminium coating), only a few aluminium strips (14) being designed to optimize the charge collection. A different method exploiting the excellent performances of this detector but requiring two successive scans, allows to discriminate the contribution of the surface sensitive conversion photoelectrons against the radiative contribution, i.e. that of the X-ray fluorescence emission which contains structural information on the bulk sample.

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Electron detector device for spectroscopic analyses of surfaces under X-ray excitation

This invention refers to an electron detector device optimized for structural surface analyses using X-ray excitation spectroscopy. The device, operated under vacuum conditions, comprises basically a large size silicon diode that can detect both the X-ray fluorescence photons and the conversion electron resulting from the irradiation of the sample by the incident X-ray photons.

The absorption of X-ray photons by a sample results in a variety of radiative/non-radiative secondary emissions which can be exploited in order to reveal structural information on the bulk sample but also, under appropriate circumstances, on its surface. In particular, X-ray absorption fine structures ("XAFS" spectra, as referred to in the scientific literature) are classically measured by monitoring the intensity of the X-ray fluorescence photons, or the intensity of the conversion electrons as a function of the energy of the monochromatic exciting X-ray beam. This requires, however, some suitable detector. The detector output signal associated with each energy data point is digitized and stored in a computer memory. The whole XAFS spectrum (corresponding to a complete scan of the monochromator) is finally reconstructed and analyzed according to more or less standard procedures so as to recover the structural information.

The secondary emissions are most often collected within a restricted solid angle along a detection axis rotated by about 90° with respect to the incident X-ray beam exciting the sample. Standard detectors will respond not only to the conversion electrons, but also to the X-ray fluorescence photons, and, even worse, to a "variable" background of X-ray photons directly scattered or diffracted by the sample. The latter

scattering background has to be removed anyway, whereas the X-ray fluoresence signal contains information or structural features of the bulk of the sample. Only the conversion electrons carry surface sensitive information.

The primary aim of the invention is to eliminate any radiative contribution and thus to enhance the "near-surface sensitivity" of the structural information.

This aim is achieved by a detector device as defined in claim 1. The method for operating such a device is defined in claim 7. This method relies on spectral differences and is inherently most sensitive to any non-linearity in the detection system: this is a fairly remarkable advantage of the invention that its linearity is excellent under the proposed conditions of operation.

The invention will now be described in detail by means of a preferred embodiment and with reference to the appended drawings.

Figure 1 shows a schematic top-view of a device corresponding to the invention.

Figure 2 presents a functional diagram of a photodiode used in the detection device shown in Figure 1.

Figure 3 is a top view of the photodiode considered in Figure 2.

Figure 4 reproduces typical experimental spectra recorded with a device corresponding to the invention. These spectra contain all the desired near-surface structural information. In this particular experiment, the sample was bulk tungsten metal with an oxidized overlayer.

Referring now to Figure 1, the sample 1 is suspended from a sample holder (not shown) inside a vacuum tight sample chamber 2 which also incorporates the whole detector assembly. An electrostatic screen 3, made of preformed copper foils or metallic grids, is disposed all around the sample except in the direction of the detector. An entrance slit 4 is cut into this electrostatic screen in order to allow the incident X-ray

beam to strike the surface of the absorbing sample 1. The plane of incidence of the exciting X-ray beam is set horizontal in the proposed experimental arrangement: this is usually preferable in terms of polarization of the incident beam but, alternatively, it could be set vertical as well (with only minor mechanical modifications).

The detection assembly itself is set always perpendicular to the plane of incidence of the exciting X-ray beam impinging on the sample at about 90° from the direction of the X-ray beam. The first element of the detector assembly is a microchannel plate 5 set vertically. It is held in a support frame 6 machined from a highly insulating material (e.g. teflon), which carries also a large size photodiode 9 which is a non-standard component described below with reference to Figures 2 and 3 and which is the heart of the detection system.

The primary function of the microchannel plate (MCP) 5 is to pre-amplify the signal of the conversion electrons. It is operated at a very low difference of potential between the polarization terminals 7 and 8, i.e. about 500 eV which results in a very modest gain (<1000) compared to the standard operation mode recommended by the channel plate manufacturers and corresponding to typical gains of 10^5 to 10^8. Under such operating conditions, the MCP 5 presents an extremely linear amplification characteristic which is essential for the present application. A further amplification is obtained by accelerating the intensified electron beam leaving the MCP before these electrons reach the photodiode. This is because the number of electron/holes pairs generated in silicon is directly proportional to the kinetic energy of the incident particles (i.e. 3.6 eV in average are required to generate an electron/hole pair). The charges created in the depleted zone of the semiconductor junction are carefully collected and result in a current of very low intensity (typically 10^{-9} to 10^{-13}A) which is measured with an ultra-low noise electrometer (not shown). Again, the linearity of the signal delivered by the

Si-diode is very high; it corresponds to at least 5 orders of magnitude in dynamic range. The signal delivered by the Si-diode is systematically normalized against the intensity variations of the X-ray beam striking the sample.

The mode of operation of the device sketched in Figure 1 is described below and involves two successive scans. The potentials of the various components are as follows:

First scan:	Second scan:
Sample: -2400 V	Sample: ground potential
Screen: -2450 V	Screen: ground potential
MCP terminal 7: -1900V<U<1500V	MCP terminal 7: -1900V<U<1500V
MCP terminal 8: -1000 V	MCP terminal 8: -1000V
Si-diode front-face: 0 V	Si-diode front-face: 0 V
Si-diode back-face: ground	Si-diode back-face: ground

The distance between the sample 1 and the MCP 5 may be, for example, 60 mm; the distance between the MCP 5 and the Si-diode may be 5 mm.

When the X-ray beam strikes the sample 1 through the entrance slit 4, the major part of it is photoabsorbed by the sample, whereas some X-ray photons may also be scattered elastically (Thomson scattering) or inelastically (Compton scattering) in the direction of the detector. Secondary emissions associated with the photoabsorption process include both conversion photoelectrons and X-ray fluorescence photons. Given the small escape depth of the conversion photoelectrons, the latter carry surface sensitive spectral information, wheras the X-ray fluorescence photons emanate from both the bulk sample and from the surface overlayer.

When reaching the MCP 5, the radiative emission (i.e. X-ray scattering + X-ray fluorescence) is entirely absorbed but a quite significant amount of secondary electrons can still be generated inside the channels and be amplified together with the conversion photoelectrons which are of direct interest for the required analyses. As a result, the measured XAFS spectrum recorded at the output of the Si-diodes is "pol-

luted" and distorted by signatures which are due to the radiative emission and not relevant to the surface of the sample. At this stage, there is nothing that can be done in order to discriminate between the respective contributions of the conversion photoelectrons and of the radiative emission.

This is why a second measuring scan is absolutely necessary. Note that both the sample and the electrostatic screen are grounded so that the conversion photoelectrons emitted by the sample, which have a low energy, have now an extremely low probability to reach the MCP 5. As a consequence, the signal delivered by the detector assembly (i.e. MCP + Si-diode) is nearly entirely due to the radiative contribution which remains unaltered. By simply substracting the normalized XAFS data of the second scan from the normalized XAFS data of the first scan, it becomes possible to isolate the contribution associated with the conversion photoelectrons and which is truly surface sensitive.

Of course, this substraction procedure is particularly demanding from the quality of the detector which should add only very little noise and also needs to be extremely linear in order to avoid spectral distorsions.

Figure 4 reproduces the characteristic FT spectrum, of the XAFS data measured during the first scan (dashed line) and the FT spectrum corresponding to the difference discussed above (continuous line): a detailed interpretation of these spectra would fall far beyond the scope of the present disclosure but it is clearly apparent that a strong signature associated with the metallic tungsten substrate (i.e. the W...W interatomic distance) is missing in the difference spectrum which is left with the only contribution of the oxide overlayer. Figure 4 is thus a good illustration of the typical "contamination" of the structural information contained in the surface sensitive contribution of the conversion photoelectrons by spectral features due to the bulk sample and resulting from the unwanted X-ray fluorescence contribution.

Given the essential role of the detector in these experiments, this detector will be described by way of example hereafter, starting with the "key component" which is the Si-diode. It is made of a high resistivity n-type silicon wafer (280 µm thick; 53x53 mm^2). As summarized in Figure 2, the junction results from the creation of a ion implanted p^+ layer 11, the interface zone between the n-type substrate 10 and the p^+ layer 11 constituting the space charge region 12. The thickness of the p^+ layer 11 is about 1300 Å. There is no additional dead layer of passivated SiO_2 as in most commercially available photodiodes or charge coupled devices (CCD): all what needs to be taken into account is the unavoidable - but extremely thin overlayer (15-30 Å) of native oxide on top of the p^+ layer 11; there is also a thin passivated strip of SiO_2 13 surrounding the periphery of the active area.

Contrary to conventional silicon photodiodes, the active area of the front face is not coated with a protective aluminium layer: there are only provided a narrow peripheral strip plus a few axial strips 14 projecting therefrom towards the center of the free surface (see Figure 3). The aluminium strips disposed as described above are required to collect the detected charges and allow electrical contacts to be taken using ultra-sonic wire bonding techniques. The whole back face can be protected with an aluminium coating. Connections can then be made from both faces with a low noise electrometer (not shown) used for ultra-low current measurements.

Since the electron penetration depth in silicon is very small, even for accelerated electrons with a kinetic energy of 1 keV, the thickness of the p^+ layer 11 has to be minimized: this is because the charges created in this p^+ layer need to diffuse to reach the junction with some probability to recombine without inducing any current detected by the electrometer. No SiO_2 nor aluminium protective coatings are provided. However, due to the absence of such an overall protective layer on top of the active area, special care must be taken

during operation: this means that the diode has to be kept under vacuum (just as the MCP!) and that water condensation and adsorption on the cold front face is not tolerated. On the other hand, the absence of SiO_2 overlayer minimizes the risk of damaging the junction when intense beams of electrons strike the active area: this is because, as established over the recent years, fixed charges tend to accumulate in the oxide and generate strong electric fields destructing the junction. This consideration may lead to protect the passivated SiO_2 strip 134 with a special teflon frame not shown in Figures 1 and 2. The very thin overlayer of native oxide on top of the p^+ layer 11 does not induce any notable degradation of the diode characteristics, e.g. any spectacular increase of the "dark" current.

It is strongly recommended to operate the Si-diode at low temperature, typically at 150 K, in order to reduce the dark current generated in the diode but also in order to increase the equivalent shunt resistor of the diode which has to be made as large as possible so as to minimize the noise due to the residual offset voltage of the J-FET used as input stage of the electrometer (not discussed in this document). This implies that the detector should preferably be operated under good vacuum.

The components of the detector asembly are all bakeable under a good primary vacuum at 400 K. Thus, the detector is compatible with the conventional ultrahigh vacuum (UHV) requirements. This is a serious advantage of the present device over many classical detectors which do not survive high temperatures involved during the baking operation of the sample chamber/detector prior to use.

The active area of the photodiode 9 and of the MCP 5, i.e. ca 25 cm^2, is quite large compared to other detectors. This is a valuable advantage for collecting the X-ray fluorescence photons properly and assign unambiguously the signatures due to the bulk. For other applications, it may be profit-

able to reduce the size of the detector (e.g. active area = 3 cm^2) in order to make the detector more compact and limit the diode capacitance; this is clearly desirable for operating the detector in the photoconductive regime with ac signals, e.g. when the incident X-ray beam is chopped at mechanical frequencies. Of course, in the latter case, the dc electrometer used in the photovoltaic regime needs to be replaced by a very sensitivie ac device (not shown).

The invention is not restricted to the embodiment as shown in the appended drawings. Without leaving the scope of the invention, the discrete values indicated above for the potentials, MCP/diode active area may be varied, though it is necessary to capture and accelerate the conversion photoelectrons while it is advisable to keep the backface of the diode at ground potential. Also quite an obvious extension of the present invention consists in inserting in front of the detector assembly a grid 15 set at some appropriate negative potential V_G on which an ac blocking potential V_B (e.g. +300V) can be superimposed (e.g. V_G = - 2250 V $\pm$ 300 V): in this configuration the conversion photoelectrons emitted by the sample are synchroneously accelerated and blocked depending on the value of V_B and the ac component of the signal delivered by the Si-diode should be directly proportional to the surface sensitive contribution of the conversion photoelectrons.

It is noteworthy that the operation of the device without the pre-intensifying MCP proved also to be quite possible in cases where the signal is very large. This simplification may find useful applications when the experiment is coupled to very intense synchrotron radiation X-ray sources of the 3rd generation.

CLAIMS

1. An electron detector device for spectroscopic analyses of surfaces under monochromatic X-ray excitation, characterized in that it comprises:
- a silicon diode (9) which is able to detect with some gain accelerated secondary electrons,
- a microchannel plate (5) used at low gain intended to pre-amplify the conversion photoelectrons emitted by the sample (1),
- an electrostatic screen (3) surrounding the space between the sample and the MCP and intended to be set at some appropriate potential.

2. A detector according to claim 1, characterized in that the silicon diode (9) is made of high resistivity n-type silicon with a ion implanted p^+ layer (11) which is about 1300 thick.

3. A detector according to claim 2, characterized in that the diode (9) has no dead layer of passivated SiO_2 but simply a thin passivated strip of SiO_2 (13) surrounding the periphery of the active area and which is protected against damageable charging by a teflon frame.

4. A detector according to claim 3, characterized in that the diode (9) has no protective aluminium coating of the active area but a few aluminium strips (14) disposed so as to collect the detected charges and allow electrical contacts to be established.

5. A detector according to claim 2 or 3 or 4, characterized in that the diode (9) is associated with a cooling means so that the diode can operate at 150 K.

6. A detector according to any one of claims 1 to 5, charac-

terized in that a grid (15) is disposed between the microchannel plate (5) and the sample (1).

7. A method for operating a device according to any one of claims 1 to 6, characterized in that two successive scans are recorded under vacuum conditions:
- during the first one, a negative potential is applied to the sample (1) and to the screen (3) with respect to the entrance face of the microchannel plate (5) and the silicon diode, with the consequence that the diode is sensitive to both the pre-intensified conversion photoelectrons and also to secondary electrons created in the microchannel plate (5) by the X-ray fluorescence photons;
- during the second scan, the sample (1) and the screen (3) are both connected to ground thereby allowing the silicon diode to detect only the secondary electrons created in the microchannel plate (5) by the X-ray fluorescence photons, the difference between both sets of data being signficative for the contribution of the conversion photoeletrons which carry structural information relative to the surface of the sample (1).

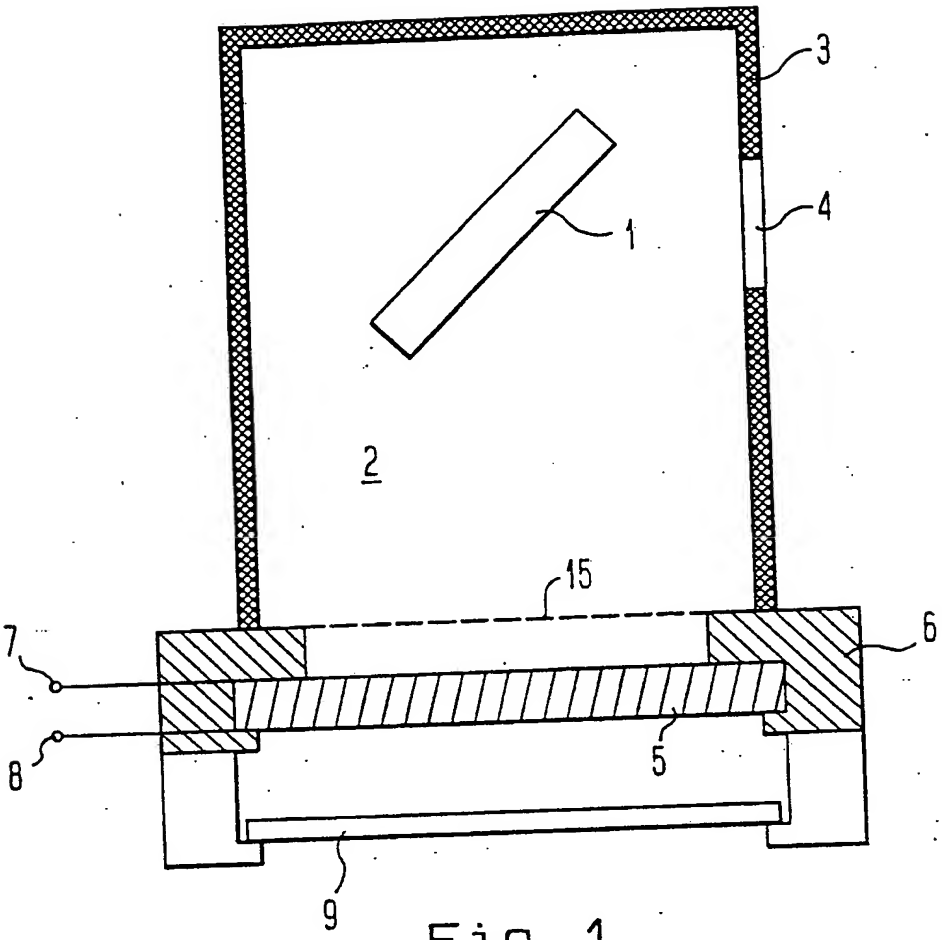

Fig. 1

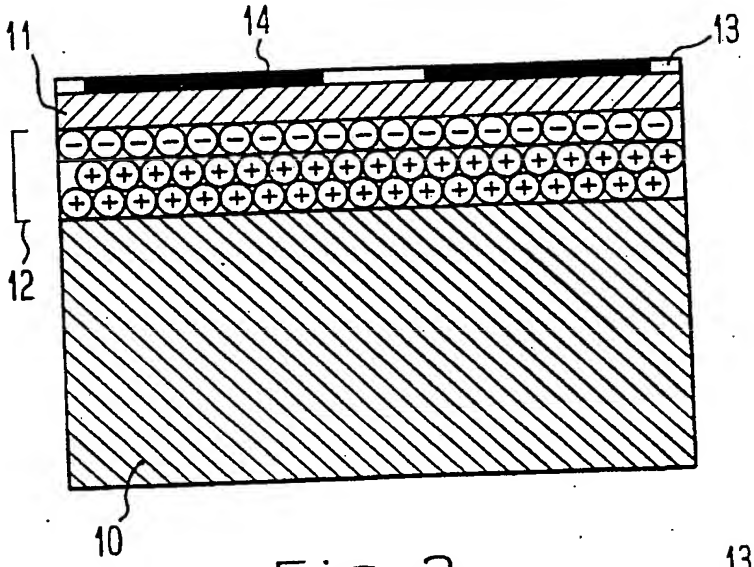

Fig. 2

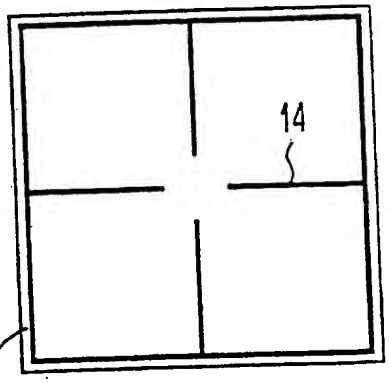

Fig. 3

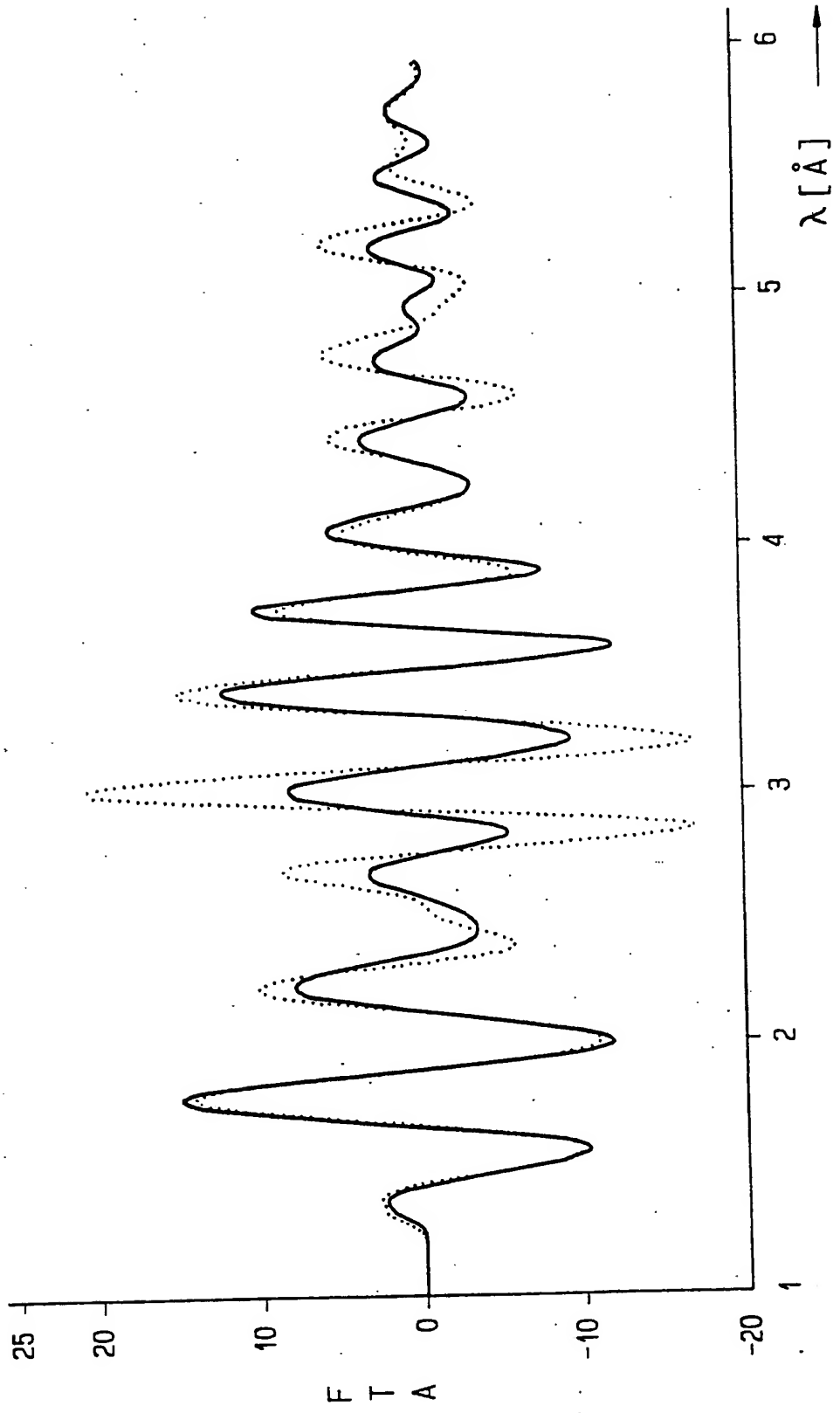

Fig.4

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G01N23/227; G01T1/24

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G01N ; G01T ; H01J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	NUCLEAR INSTRUMENTS AND METHODS. vol. A281, no. 1, 20 August 1989, AMSTERDAM NL pages 128 - 132; H. YAMAMOTO ET AL.: 'LOW-ENERGY NUCLEAR RADIATION DETECTION WITH A SILICON PHOTODIODE' see page 128 - page 132 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 6, no. 15 (P-134)(1030) 12 August 1982 & JP,A,57 072 072 (FUJITSI K.K.) 6 May 1982 see abstract ---	1

[o] Special categories of cited documents :[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11 MAY 1992	20. 05. 92
International Searching Authority	**Signature of Authorized Officer**
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Form PCT/ISA/210 (second sheet) (January 1985)